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Study on Anharmonic Effect of the Unimolecular Reaction of $CH_2(D_2)FO$

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Study on the unimolecular reaction for CH_2FO and CD_2FO is carried out. The structures, energy barriers and zero point energy of the three channels in the title unimolecular reactions are computed with the MP2/6-311++G(3df, 3pd) method. RRKM theory is used to calculate the rate constants of canonical case at temperature range of 500–5000 K and microcanonical system at total energy of 19.05–71.68 kcal/mol. The results indicate that the anharmonic effect and isotope effect are very small for the three channels, and the anharmonic rate constants, around 10^9–10^{11} s^{-1}, are close to the experimental prediction reasonably.

Key Words : RRKM theory, Rate constant, Anharmonic effect, Isotope effect, Unimolecular reaction

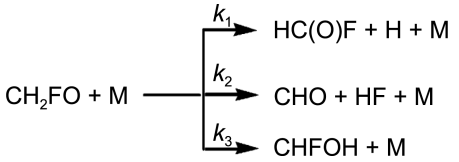
Introduction

Research on the alkoxy radicals draws increasing interest due to its important intermediates in combustion and atmospheric chemistry. As far as we concerned, numerous experiments have been done on methoxy and chloroalkoxy radicals, but few information is available on halogen-substitued alkoxy radical, flouromethoxy, CH_2FO.[1-4] Recently, lots of studies indicate that fluoromethoxy and hydroflourocarbon chemistry have become very important in a variety of areas including atmospheric chemistry, combustion suppression, and plasma etching in the microelectronics industries. The investigation of the reactant of CH_2FO may be of practical value as well as fundamental interest. The CH_2FO radical is an important intermediate in the oxidation of CH_3F(HFC-41).[4] Just like most alkoxy radicals, the primary atmospheric fact of CH_2FO is an unimolecular reaction, besides the reaction with O_2:[5]

$$CH_2FO + M \rightarrow \text{products} + M$$

As far as we know, there has been no accurate kinetic data on this reaction.

In this study, we focus our attention on the three unimolecular channels of the title reaction:



The purpose of this paper is to calculate the rate constants of the unimolecular reaction of CH_2FO and CD_2FO radicals according to RRKM theory and transition state theory and discuss the anharmonic effect and isotope effect. The Morse oscillators (MOs) are employed in the calculation for convenience. The Yao and Lin (YL) method is used to compute the rate constants and the microcanonical and canonical cases give similar results for the rate constant in this paper.

Calculation Methodology

***Ab initio* Calculation.** In this paper, the three reaction channels for the unimolecular dissociation are examed:

$$CH_2FO + M \rightarrow HC(O)F + H + M$$

$$CH_2FO + M \rightarrow CHO + HF + M$$

And the unimolecular isomerization:

$$CH_2FO + M \rightarrow CHFOH + M$$

The geometries of the reactants, products, various intermediates and transition states have been gradually optimized, with 6-311++G(3df, 3pd), by the HF, B3LYP, MP2 method. Vibrational harmonic and anharmonic frequencies, calculated at the same level, are used for the characterization of stationary points, transition state point and zero-point-energy correction as well as the calculations of the reaction rate constant. To achieve higher accuracy and reliability, the single point energies are recalculated by way of employing the coupled cluster CCSD(T) method with 6-311++G(3df, 3pd) basis set. The GAUSSIAN 03 programs are utilized for all *ab initio* calculations.[6]

RRKM Theory and Anharmonic Effect. Recent reviews of the anharmonic effect on unimolecular reactions can be found in refs 7-18. According to the RRKM theory, for the microcanonical system, the rate constant for unimolecular reaction can be expressed as[19]

$$k(E) = \frac{\sigma}{h}\frac{W^{\neq}(E - E^{\neq})}{\rho(E)} \quad (1)$$

where σ is the symmetry factor (here we set $\sigma = 1$), h is Planck's constant, $\rho(E)$ represents the density of the state of the reactant, $W^{\neq}(E)$ stands for the total number of states for the transition state, E and $E^{\neq}$ are the total energy and the activation energy in the microcanonical case.

The definition of $W(E)$ and (E) can be expressed as

$$W(E) = \sum_i H(E-E_i) \tag{2}$$

and

$$\rho(E) = \frac{dW(E)}{dE} \tag{3}$$

where $H(E-E_i)$ denotes Heaviside function, E_i are energy levels.

Laplace transformation is employed for $W(E)$ and $\rho(E)$, we obtain

$$\int_0^\infty dE e^{-\beta E} W(E) = \frac{Q(\beta)}{\beta} = L[W(E)] \tag{4}$$

$$\int_0^\infty dE e^{-\beta E} \rho(E) = Q(\beta) = L[\rho(E)] \tag{5}$$

where $\beta = 1/kT$, k is Boltzmann's constant, T is the temperature of the system, and $Q(\beta)$ is the partition function of the system. That is, once $Q(\beta)$ are obtained, $W(E)$ and $\rho(E)$ can be determined by using above equations or inversing Laplace transformation. More details can be found in ref 20.

For a canonical system, the rate constant $k(T)$ for unimolecular reaction is given by[21-24]

$$k(T) = \frac{kT}{h}\frac{Q^{\neq}(T)}{Q(T)} e^{-\frac{E^{\neq}}{kT}} \tag{6}$$

where k is Boltzmann's constant, T is the temperature of the system, and $Q(T)$ and $Q^{\neq}(T)$ are the partition functions of the reactant and the activated complex, respectively. In this case, we obtain

$$Q^{\neq}(T) = \prod_i^{N-1} q_i^{\neq}(T) \tag{7}$$

$$Q(T) = \prod_i^{N} q_i(T) \tag{8}$$

where N is the number of the vibrational modes of the reactant, $q_i^{\neq}(T)$ and $q_i(T)$ represent the vibrational partition functions of the activated complex and the reactant, respectively.

The above discussions show that the partition function is important in the calculation of $k(E)$ and $k(T)$. To calculate the partition function, MO is applied, and the energy of the i-th vibrational mode can be expressed as follow:

$$E_{n_i} = \left(n_i + \frac{1}{2}\right)\hbar\omega_i - x_i\left(n_i + \frac{1}{2}\right)^2 \hbar\omega_i, \tag{9}$$

where n_i and ω_i are the vibrational quantum number and the frequency of the i-th vibrational mode, respectively. x_i is MO parameter, and it can be expressed as: $x_i = \frac{\hbar\omega_i}{4D_{ie}}$, where D_{ie} represents the well depth of MO. In this study, x_i is obtained from anharmonic frequencies calculated by Gaussian 03 program.

Results and Discussion

The energetic profile diagram (Figures 1 and 2) shows the CCSD(T)/6-311++G(3df, 3pd) energies of the three transition states and three sets of products relative to the ground-state energy of $CH(D)_2FO$, arbitrarily taken as zero. Figure 3 shows the optimized geometries, the calculated bond lengths and bond angles, the transition states of the three channels. For the product (HC(O)F, CHO, HF), the experimental optimized geometries and data are quite close to the theoretical ones.[25-27] The largest deviation of bond length and bond

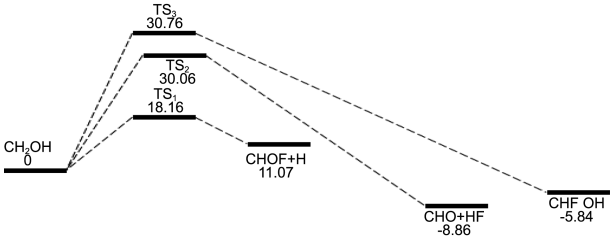


Figure 1. Energetic profile for the potential energy surface of the unimolecular reaction of CH_2FO at the CCSD(T)/6-311++G(3df, 3pd) level of theory.

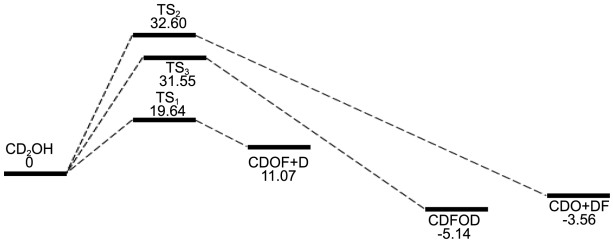


Figure 2. Energetic profile for the potential energy surface of the unimolecular reaction of CD_2FO at the CCSD(T)/6-311++G(3df, 3pd) level of theory.

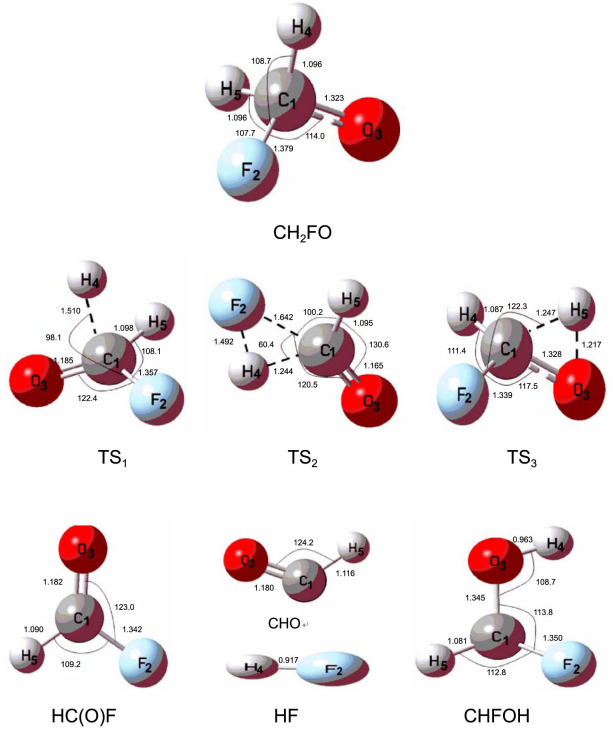


Figure 3. Optimized geometries of the stationary points of the title reaction.

angle is 0.012 Å for C-H of HC(O)F and 1.5° for FOC of HC(O)F, respectively, at the MP2/6-311++G(3df, 3pd) level of theory. When it comes to the reactant (CH_2FO) and its isomer (CHFOH), there is no accurate theoretical data to be compared with, thus, we are supposed to utilize the provided results in ref 28. The structures are in good agreement with the given one.[28] The largest deviation of the bond angle and bond length is 1.5° for COH of CHFOH and 0.08 Å for C-F of CH_2FO, respectively. The optimized geometries from the level of MP2/6-311++G(3df, 3pd) meet the agreement of the available experiment data,[28] and the results at the MP2/6-311++G(3df, 3pd) level of theory as accurate as those from the MPW1K/6-31+G(d, p) and the QCISD/6-311+G(d, p) method.[28]

For transition states (TS_1, TS_2, TS_3), there are some slight differences between the calculated results and the available experimental data[25-28] in bond angles and bond lengths. For instant, comparing to the available data,[25-28] the active bonds, C_1-H_5 of TS_1, C_1-F_2, C_1-H_5, F_2-H_5 of TS_2, C_1-H_5, O_3-H_5 of TS_3, from the MP2/6-311++G(3df, 3pd) method, is not as accurate as the others of TS_1, TS_2 and TS_3, C_1-H_5 of TS_1, respectively. But it can be seen from Figure 1 that, except for the active bond, the lengths of the other bonds are quite similar to the ones of product (HC(O)F). As the respect of TS_2, TS_3, the similar characteristics also appear, yet not as notable as TS_1. Just like what Qiong Luo and Qian Shu Li said,[28] TS_1 can be described as simple H-C bond rupture. In case of TS_2, the geometry is best described as a 1, 2 shift of F across the H_5-C_1 bond of CH_2O. Considering that the geometries of TS_3 and TS_2 are alike, TS_3 can also be described as a 1, 2 shift of H across the O_3-C_1 bond of CHFO.[28] The same calculation are given in CD_2FO reaction, which gives the similar structures and results.

For the unimolecular dissociation of the CH_2FO radical, the geometric and the energetic parameters of the reactant and transition stats are collected in Table 1. The harmonic vibrational frequencies of the reactant and transition states are in good agreement with the experimental values and theoretical results given in reference 28, at the MP2/6-311++G(3df, 3pd) level of theory. We recomputed the single point energies at the CCSD(T)/6-311++G(3df, 3pd) level, then obtained more accurate values of the single point energies for each channel, namely 18.16, 30.03 and 30.76 kcal/mol, respectively.

TS1. To calculate the above-mentioned energy, we illustrated the relation between the total energy of a microcanonical system and the temperature of a canonical system means

$$E = -\left[\frac{\partial \ln Q}{\partial \beta}\right] \tag{10}$$

with the equation. The energy in the microcanonical system can be given, which are listed in Table 2.

Table 1. Parameters used in rate constant calculations, obtained from MP2/6-311++G(3df, 3pd) level. The barriers are computed at the CCSD(T)/6-311++G(3df, 3pd) level.

	CH_2FO	TS1-H	TS2-H	TS3-H
Zero-point energy (Hartree)	0.0311786	0.0238254	0.0254663	0.0268406
Total energies (Hartree)	–214.0219731	–213.985687	–213.9674035	–213.8687172
SPE (Hartree)	–213.9907945	–213.9618616	–213.9429372	–213.9417766
Barrier (kcal/mol)		18.16	30.03	30.76
	CD_2FO	TS1-D	TS2-D	TS3-D
Zero-point energy (Hartree)	0.024637	0.019645	0.0208324	0.0216584
Total energies (Hartree)	–214.0219731	–213.985687	–213.96621	–213.9687172
SPE (Hartree)	–213.9973361	–213.966042	–213.9453776	–213.9470588
Barrier (kcal/mol)		19.64	32.60	31.55

Table 2. The rate constant of the TS_1 at different temperature for canonical system, calculated at MP2/6-311++G(3df, 3pd) level. The units of temperature, total energy and rate constant are K, kcal/mol, s^{-1}

Temperature (K)	500	1000	1500	1800	1900	2000
Total energy (kcal/mol)	1.18	6.14	12.96	17.49	19.05	20.63
Harmonic rate constant (H)	1.41×10^{5}	2.94×10^{9}	8.86×10^{10}	3.02×10^{11}	4.13×10^{11}	5.07×10^{11}
Anharmonic rate constant (H)	1.41×10^{5}	2.87×10^{9}	8.86×10^{10}	2.83×10^{11}	3.84×10^{11}	5.07×10^{11}
Harmonic rate constant (D)	3.59×10^{4}	1.51×10^{9}	5.79×10^{10}	1.98×10^{11}	3.00×10^{11}	3.66×10^{11}
Anharmonic rate constant (D)	3.61×10^{4}	1.51×10^{9}	5.69×10^{10}	1.93×10^{11}	2.66×10^{11}	3.56×10^{11}
Temperature	2500	3000	3500	4000	4500	5000
Total energy	28.75	37.11	45.63	54.25	62.94	71.68
Harmonic rate constant (H)	1.61×10^{12}	3.33×10^{12}	5.62×10^{12}	8.33×10^{12}	1.13×10^{13}	1.45×10^{13}
Anharmonic rate constant (H)	1.45×10^{12}	2.90×10^{12}	4.73×10^{12}	6.76×10^{12}	8.85×10^{12}	1.09×10^{13}
Harmonic rate constant (D)	1.12×10^{12}	2.36×10^{12}	4.02×10^{12}	6.02×10^{12}	8.23×10^{12}	1.06×10^{13}
Anharmonic rate constant (D)	1.08×10^{12}	2.25×10^{12}	3.81×10^{12}	5.63×10^{12}	7.60×10^{12}	9.50×10^{13}

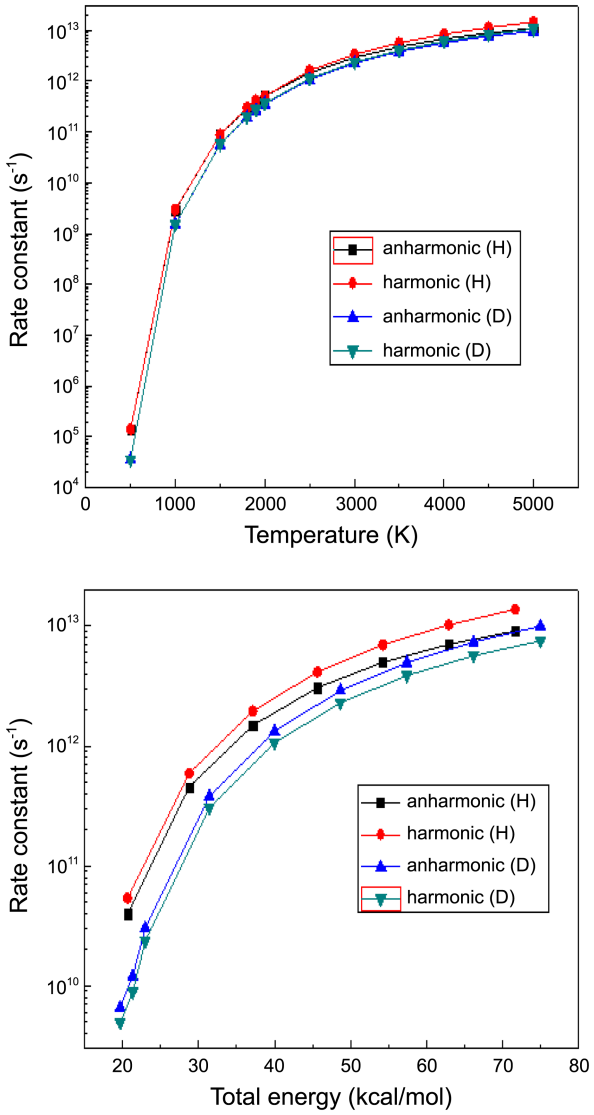


Figure 4. The canonical and microcanonical rate constant of the TS_1. The units of rate constant is s^{-1}.

The harmonic and anharmonic rate constant for the canonical system are shown in Table 2, with the temperature ranging from 500 K to 5000 K. Meanwhile, those rate constants are also displayed in Figure 4. It is obvious that, within the scope of 500 K-1800 K, the energies are lower than the calculated activation energy, *i.e.* 18.16 kcal/mol. Thus, the rate constant in a microcanonical system at the higher energy have to be calculated.

In Table 3, we also give the harmonic and anharmonic rate constant of the microcanonical system at various calculated energy. From Tables 2 and 3, Figure 4, we can conclude that in the canonical case, the harmonic rate constants which increase sharply from 1.41×10^5 to 1.45×10^{13} s^{-1} with the temperature ranging from 500 to 5000 K are slightly higher than the anharmonic ones which increase from 1.41×10^5 to 1.09×10^{13} s^{-1}. Meanwhile, in respect of microcanonical case, it does the same matters. The rate constants of the anharmonic effect increasing sharply from 1.56×10^{10} to 9.02×10^{12} s^{-1} with the energy ranging from 19.5 to 71.68 kcal/mol are lower than the harmonic ones increasing from 2.37×10^{10} to 1.37×10^{13} s^{-1}, the distinction of which becomes more obvious in higher temperature. In addition, compared with the canonical case, the harmonic effect is more sensitive in the microcanoical case. Furthermore, it can be easily figured out that in whichever point shown in Figure 4, the rate constants of the microcanonical case are higher than the ones of the canonical case.

TS_2. Similar to the channel 1, the energy in the microcanonical system can be calculated using Eq. (10). This means that we have to calculate the rate constant in a microcanonical system at the energies larger than the calculated activation energy, *i.e.* 30.06 kcal/mol. The harmonic and anharmonic rate constants for the canonical system are shown in Table 4, with the temperature ranging from 500 K to 5000 K. While in Table 5, the harmonic and anharmonic rate constants of the microcanonical system are shown at various calculated energy.

From Table 4 and Figure 5, an obvious distinction of changing rules exists in the rate constant between TS1 and TS3. At the beginning, the anharmonic rate constants which are from 1.21×10^7 to 7.35×10^{11} s^{-1} with the temperature ranging from 500 to 3500 K are increasing more evidently than the harmonic ones which are from 9.20×10^{-1} s^{-1} to 7.28×10^{11} s^{-1}, while with the temperature ranging from 3500 to 5000 K, we can see the intersection clearly. The harmonic rate constants which are from 1.32×10^{12} s^{-1} to 3.02×10^{12} s^{-1} become higher than the anharmonic ones which are from 1.01×10^{12} s^{-1} to 1.27×10^{12} s^{-1}, moreover,

Table 3. The rate constant of the TS_1 at different energies for the canonical system, calculated at MP2/6-311++G(3df, 3pd) level. The units of temperature, total energy and rate constant are K, kcal/mol, and s^{-1}, respectively

Total energy	19.05	20.63	28.75	37.11	45.63	54.25	62.94	71.68
Harmonic W(E) of TS	1.24	3.99	213.56	2699.11	18300	85400	312000	951000
Harmonic ρ(E) of reactant	1.57	2.23	10.82	41.35	132.02	366.37	909.69	2064.19
Harmonic rate constant (H)	2.37×10^{10}	5.37×10^{10}	5.92×10^{11}	1.90×10^{12}	4.10×10^{12}	6.90×10^{12}	1.00×10^{13}	1.30×10^{13}
Harmonic rate constant (D)	8.90×10^{9}	2.35×10^{10}	3.04×10^{11}	1.00×10^{12}	2.20×10^{12}	3.80×10^{12}	5.60×10^{12}	7.50×10^{12}
Anharmonic W(E) of TS	1.02	3.76	228.26	3089.53	22200	110000	427000	1390000
Anharmonic ρ(E) of reactant	1.96	2.84	14.99	62.37	217.35	661.62	1812.98	4566.02
Anharmonic rate constant (H)	1.56×10^{10}	3.97×10^{10}	4.56×10^{11}	1.49×10^{12}	3.07×10^{12}	5.00×10^{12}	7.07×10^{12}	9.11×10^{12}
Anharmonic rate constant (D)	1.20×10^{10}	3.03×10^{10}	3.79×10^{11}	1.33×10^{12}	2.90×10^{12}	4.97×10^{12}	7.39×10^{12}	1.00×10^{13}

Table 4. The rate constant of the TS_2 at different temperature for canonical system, calculated at MP2/6-311++G(3df, 3pd) level. The units of temperature and rate constant are K, kcal/mol, S^{-1}

Temperature	500	1000	1500	2000	2500	2600
Total energy	1.18	6.14	12.96	20.63	28.75	30.41
Harmonic rate constant (H)	0.92	6.64×10^{6}	1.42×10^{9}	2.14×10^{10}	1.10×10^{11}	1.42×10^{11}
Anharmonic rate constant (H)	1.21	1.16×10^{7}	2.72×10^{9}	3.90×10^{10}	1.74×10^{11}	2.17×10^{11}
Harmonic rate constant (D)	7.08×10^{-2}	1.79×10^{6}	5.62×10^{8}	1.01×10^{10}	5.75×10^{10}	7.52×10^{11}
Anharmonic rate constant (D)	9.61×10^{-2}	3.86×10^{6}	1.51×10^{9}	2.78×10^{10}	1.41×10^{11}	1.78×10^{11}
Temperature	2700	3000	3500	4000	4500	5000
Total energy	32.07	37.11	45.63	54.25	62.94	71.68
Harmonic rate constant (H)	1.80×10^{11}	3.31×10^{11}	7.28×10^{11}	1.32×10^{12}	2.09×10^{12}	3.02×10^{12}
Anharmonic rate constant (H)	2.64×10^{11}	4.27×10^{11}	7.35×10^{11}	1.01×10^{12}	1.19×10^{12}	1.27×10^{12}
Harmonic rate constant (D)	9.63×10^{10}	1.84×10^{11}	4.22×10^{11}	7.87×10^{11}	1.28×10^{12}	1.89×10^{12}
Anharmonic rate constant (D)	2.19×10^{11}	3.65×10^{11}	6.36×10^{11}	8.64×10^{11}	9.94×10^{11}	1.02×10^{12}

Table 5. The rate constant of the TS_2 radical at different energies for the canonical system, calculated at MP2/6-311++G(3df, 3pd) level. The units of temperature, total energy and rate constant are K, kcal/mol, and s^{-1}, respectively

Total energy	30.41	32.07	37.11	45.63	54.25	62.94	71.68
Harmonic W(E) of TS	1.02	2.94	45.30	865.00	7050	36600	143000
Harmonic ρ(E) of reactant	14.40	19.00	41.30	132.00	366.00	910.00	2060.00
Harmonic rate constant (H)	2.12×10^{9}	4.64×10^{9}	3.28×10^{10}	1.96×10^{11}	5.77×10^{11}	1.21×10^{12}	2.08×10^{12}
Harmonic rate constant (D)	8.81×10^{8}	2.27×10^{9}	1.49×10^{10}	8.88×10^{10}	2.63×10^{11}	5.54×10^{11}	9.58×10^{11}
Anharmonic W(E) of TS	0.80	3.66	84.70	2120.00	18000	87500	294000
Anharmonic ρ(E) of reactant	20.30	27.2	62.4	217	662	1810	4570
Anharmonic rate constant (H)	1.18×10^{9}	4.04×10^{9}	4.07×10^{10}	2.92×10^{11}	8.18×10^{11}	1.45×10^{12}	1.93×10^{12}
Anharmonic rate constant (D)	5.64×10^{8}	1.54×10^{9}	1.05×10^{10}	6.20×10^{10}	1.79×10^{11}	3.66×10^{11}	6.10×10^{11}

the distinction of which becomes obvious in the higher temperature. In Figure 5, the same tendency can be found that the intersection exists in both lower and higher total energy and the rate constants of harmonic and anharmonic in microcanonical case alternately rise. The difference is caused by using the different models, harmonic and anharmonic potentials, which are utilized to simulate the vibrational bonds. For the different models and different vibrational states, the total number of states and density of states are counted, which affects the dissociation rate constant. It should be noted that the differences in the dependence of harmonic and anharmonic rate constants upon the temperature are due to the harmonic surfaces and anharmonic surfaces in the RRKM calculations of the rate constants and the anharmonic oscillator (obtained from the corresponding anharmonic surfaces) will have nonequal energy spacings, decreasing with the increasing quantum numbers and its vibrational quantum numbers have a maximum limit.

TS_3. Similar to the channels 1 and 2, the energy in the microcanonical system can be calculated using Eq. (10). This means that we have to calculate the rate constant in a microcanonical system at the energies larger than the calculated activation energy, *i.e.* 30.76 kcal/mol. Thus, we calculated the harmonic and anharmonic rate constants for the canonical and microcanonical systems. The rate constants for the canonical system are shown in Table 6 and Figure 6, with the temperature ranging from 500 K to 5000 K. In Table 7, we also give the harmonic and anharmonic rate constants of the microcanonical system at various calculated energy.

From Table 5 and Figure 6, we can conclude that in the canonical case, the harmonic rate constants which are from 3.96×10^{-1} to 1.90×10^{12} s^{-1} with the temperature ranging from 500 to 5000 K are slightly higher than the anharmonic ones which are from 3.94×10^{-1} to 1.27×10^{12} s^{-1}. And in the microcanonical case, the rate constants of the anharmonic effect, which increasing sharply from 1.47×10^{9} to 8.15×10^{11} s^{-1} with the energy ranging from 32.07 to 71.68 kcal/mol are lower than the ones of the harmonic effect increasing from 2.48×10^{9} to 1.31×10^{12} s^{-1}, moreover, the distinction of which becomes more obvious in the higher temperature. In addition, compared with the canonical case, the anharmonic effect is more sensitive in the microcanoical case. Furthermore, it can be easily figured out that in whichever the point shown in Figure 4 is the rate constants of the canonical case are higher than the microcanonical case ones.

Above all, it is clear that the anharmonic effect has very little influence on the reactions of the three channels of CH_2FO. The values of anharmonic rate constants and harmonic rate constants are closer for the unimolecular isomerization reactions of the CH_2FO radical both in the canonical system and the microcanonical system. What's more, both the anharmonic and isotope effect take the common influence on the canonical and microcanonical cases. The rate con-

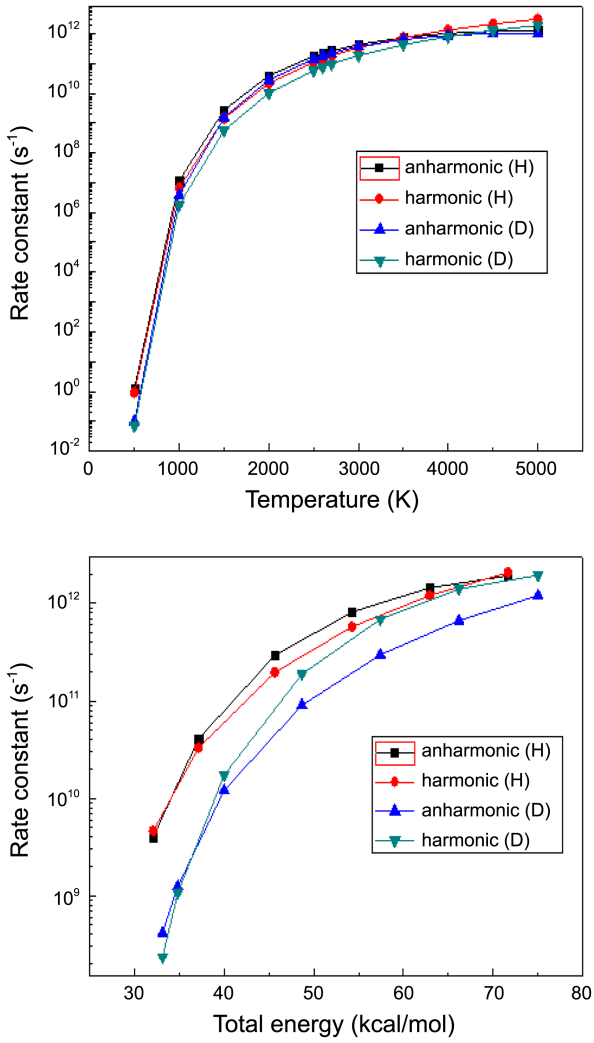


Figure 5. The canonical and microcanonical rate constant of the TS_2. The units of rate constant is s^{-1}.

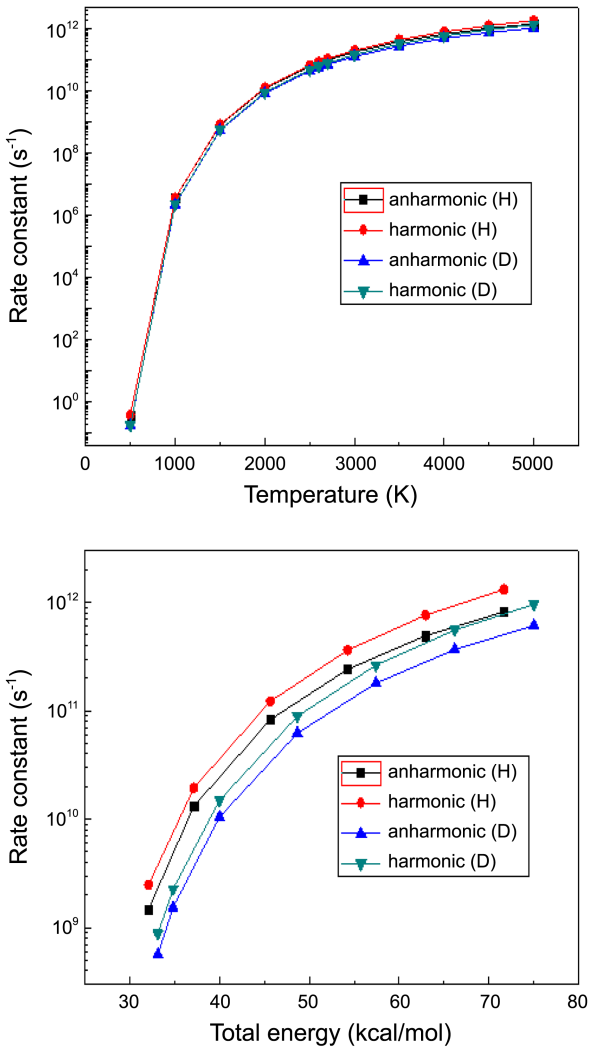


Figure 6. The canonical and microcanonical rate constant of the TS_3. The units of rate constant is s^{-1}.

stants of the unimolecular isomerization of the CD_2FO radical are also calculated and plotted in Figures 4-6. It can be seen that the CD_2FO has a similarity trend with the CH_2FO besides the rate constants of CD_2FO are a little lower than the ones of CH_2FO. For the D atomic's radius ratio is larger than H atomic's and the D atomic's quality, electronegative, is less obvious than the H atomic's, the attractive force exists between D and F is less than H and F, hence the

Table 6. The rate constant of the TS_3 at different temperature for canonical system, calculated at MP2/6-311++G(3df, 3pd) level. The units of temperature and rate constant are K, kcal/mol, s^{-1}

Temperature	500	1000	1500	2000	2500	2600
Total energy	1.18	6.14	12.96	20.63	28.75	30.41
Harmonic rate constant (H)	3.96×10^{-1}	3.76×10^{6}	8.59×10^{8}	1.33×10^{10}	6.89×10^{10}	8.89×10^{10}
Anharmonic rate constant (H)	3.94×10^{-1}	3.68×10^{6}	8.22×10^{8}	1.24×10^{10}	6.30×10^{10}	8.09×10^{10}
Harmonic rate constant (D)	1.80×10^{-1}	2.38×10^{6}	5.90×10^{8}	9.39×10^{9}	4.96×10^{10}	6.41×10^{10}
Anharmonic rate constant (D)	1.78×10^{-1}	2.31×10^{6}	5.60×10^{8}	8.72×10^{9}	4.50×10^{10}	5.79×10^{10}
Temperature	2700	3000	3500	4000	4500	5000
Total energy	32.07	37.11	45.63	54.25	62.94	71.68
Harmonic rate constant (H)	1.13×10^{11}	2.08×10^{11}	4.58×10^{11}	8.28×10^{11}	1.31×10^{12}	1.90×10^{12}
Anharmonic rate constant (H)	2.64×10^{11}	4.27×10^{11}	7.35×10^{11}	1.01×10^{12}	1.19×10^{12}	1.27×10^{12}
Harmonic rate constant (D)	8.13×10^{10}	1.51×10^{11}	3.34×10^{11}	6.06×10^{11}	9.65×10^{11}	1.40×10^{12}
Anharmonic rate constant (D)	7.30×10^{10}	1.33×10^{11}	2.87×10^{11}	5.06×10^{11}	7.79×10^{11}	1.09×10^{12}

Table 7. The rate constant of the TS_3 radical at different energies for the canonical system, calculated at MP2/6-311++G(3df, 3pd) level. The units of temperature, total energy and rate constant are K, kcal/mol, and s^{-1}, respectively

Total energy	32.07	37.11	45.63	54.25	62.94	71.68
Harmonic W(E) of TS	1.57	26.75	536.00	4420.04	23100	90200
Harmonic ρ(E) of reactant	19.00	41.35	132.00	366.37	909.69	2064.19
Harmonic rate constant (H)	2.48×10^{9}	1.94×10^{10}	1.22×10^{11}	3.62×10^{11}	7.60×10^{11}	1.31×10^{12}
Harmonic rate constant (D)	2.27×10^{9}	1.49×10^{10}	8.88×10^{10}	2.63×10^{11}	5.54×10^{11}	9.58×10^{11}
Anharmonic W(E) of TS	1.35	27.35	601.00	5321.81	29700	124000
Anharmonic ρ(E) of reactant	27.20	62.37	217.00	661.62	1812.98	4566.02
Anharmonic rate constant (H)	1.48×10^{9}	1.31×10^{10}	8.29×10^{10}	2.41×10^{11}	4.91×10^{11}	8.15×10^{11}
Anharmonic rate constant (D)	1.54×10^{9}	1.05×10^{10}	6.20×10^{10}	1.79×10^{11}	3.66×10^{11}	6.10×10^{11}

C-F bond is more firmly in CD_2FO and it is harder to break the bond C-D, and form the product.

Conclusion

A direct *ab initio* dynamics study is carried out for the thermal rate constants of the three channels of the unimolecular reaction of CH_2FO and CD_2FO. The calculated structural information is calculated at the MP2/6-311++G(3df, 3pd). Levels of theory are similar and in good agreement with the available experimental data. This suggests that the MP2/6-311++G(3df, 3pd) level of theory could provide reasonable geometric information.

In this paper, we calculate the harmonic and anharmonic rate constants of the unimolecular decomposition for alkoxy radical. The rate constants of the reaction are evaluated by using the MP2/6-311++G(3df, 3pd) and CCSD(T)/6-311++G(3df, 3pd) methods in the temperature range of 500-5000 K. The H/D elimination channel for the unimolecular reaction of CH_2/D_2FO is the dominating reaction in the whole temperature range. We observed that within both canonical and microcanonical approaches, the harmonic and anharmonic calculations give similar results. At the same time, the results show that the differences between the harmonic and anharmonic rate constants are rather small for both the canonical and microcanonical case. And also the rate constants show differences with the increasing temperatures and the total energies. Furthermore, the rate constants are very sensitive to the lower energies, while it is insensitive to the higher energies. Besides we calculate the harmonic and anharmonic rate constants of the unimolecular reaction for HFCO and DFCO radicals with the YL method in this paper, and the rate constants of DFCO radical are lower than those of the HFCO radical. These computational studies would be useful in providing further insight into the atmospheric chemistry of CH_2FO and CD_2FO, and it could be expected that further experimental studies would be encouraged on the reactions.

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